METHOD OF MANUFACTURING GERMANIUM-CONTAINING SOLUTION FROM YELLOW SOIL

BACKGROUND OF THE INVENTION

The present invention relates to a method of manufacturing germanium-containing solution from yellow soil distributed on the earth's surface, and more particularly to a method of manufacturing germanium-containing solution by heating yellow soil formed in a clod of earth to red heat and dipping the clod of the yellow soil in water, so that oxidized organic germanium-containing solution can be obtained with high efficiency, and the germanium which acts advantageously on the human body can be used environmental-friendly and economically.

Germanium is a carbon group element belonging to 4B of Periodic Table, with its atomic symbol Ge, atomic number 32, melting point 958.5°C, and boiling point 2,700°C. It is a semi-metallic element distributed widely and thinly under the earth's crust and it is found in germanite, argyrodite, and some zinc ores. It is also present in coal and is known to be present in certain plants. Germanium is stable in the air, but tends to be oxidized in a heated state to red hot.

Of the germanium distributed on the earth, mineral germanium cannot be ingested in the human body, and it is widely used in the electronic field as industrial material. On the contrary, organic germanium can be ingested in the human body with no detrimental effect and no toxicity. Recently, it has been known that the organic germanium acts advantageously on the human body, for example, by reinforcing immunity system, removing toxic substances, discharging heavy metals, promoting the flow or circulation of blood, and supplying oxygen. Therefore, the organic germanium has been widely studied and applied in various fields such as medical treatment, beauty or cosmetic treatment, health food, etc.

According to one conventional method of manufacturing germanium compounds, germanium chloride was obtained as a by-product in the process of refining sulfide minerals. That is, ores containing germanium were burned to make germanium oxide, which was then sintered by adding coal and salt to produce germanium and cadmium as volatile parts. These volatile parts were absorbed by sulfuric acid and

cadmium was removed by using zinc powder. Then, the resulting product was dried and calcined, and then distilled with hydrochloric acid to finally produce germanium chloride.

Further, according to another conventional method, sodium carbonate and lime were provided by a method of collecting briquettes in the combustion of coal, and copper oxide was added thereto, so that they were heated together. Then, the resulting slag containing germanium was powdered, and while passing chlorine, it was distilled in an aqueous solution of iron chloride by adding hydrochloric acid and sulfuric acid, so that germanium chloride was obtained.

In the above conventional methods, however, germanium was obtained as chloride compounds in a powder form. Therefore, in order to apply to the human body or for other uses, they should be processed further, and thus it was not economical and it was inevitable that their applications should be limited. Further, the manufacturing processes up to obtaining the germanium chloride were not simple, and should be proceeded with considerable care since various chemicals which could be harmful were used in the procedures.

In the meantime, Korean Patent No. 302277 (Application No. 10-1999-31010) issued on July 2, 2001 disclosed a method of manufacturing germanium-containing solution from natural germanium ores. In this conventional method, natural raw ores containing 0.36 to 1.05 germanium were pulverized to 200-250 mesh, dried at 100-110°C for 1-2 hours, cooled in the air, and sintered at 1050-1100°C for 4-5 hours. After the sintered product was cooled in the air, distilled water was added to reach the concentration of 0.5-1.0 kg/l. Then, the solution was stirred for 30-40 minutes and filtered to give the germanium-containing solution.

According to the above patented method, however, since natural germanium ores were directly used as raw materials, there could be limitation in the supply of raw materials.

Also, since the germanium raw ores had to be pulverized and sintered at high temperatures above 1,000°C, labor costs and manufacturing costs could be considerably expensive.

Further, as the pulverized germanium ores were directly extracted with the

distilled water and filtered, the resulting filtrate was obtained as a solution containing particulates. Thus, it was not suitable for use as drinking water.

BRIEF SUMMARY OF THE INVENTION

In order to solve the above disadvantages of the prior art, the present invention uses yellow soil, including the earth from a fireplace, which is commonly available from the earth's surface, as raw materials, instead of the natural germanium ores.

As used herein, the term yellow soil refers to yellow ocher or ocherous soil. It is a current trend in Korea to include the yellow soil or ocherous soil in particulate form in manufacturing electric blankets for personal use, vessels or containers, cosmetics, and many other products for its advantageous effects to the human body. As used herein, the term earth from a fireplace refers to yellow soil obtained by repeatedly heating the soil in high temperatures and cooling it in the fireplace. The fireplace is an one of the main sources from which the yellow or ocherous soil can be obtained. In old Korean society or in some rural areas these days, people made a fire in a fireplace in the kitchen for cooking and heating, and the fireplace was provided with the ocherous soil therein. Since the fire was repeatedly lighted almost every day for cooking and heating, the ocherous soil can be obtained from the inside of the fireplace as a result of repeated heating and cooling. The term "earth from a fireplace" means this ocherous soil obtained as such. According to a published literature, the earth from the fireplace is an effective treatment of vertigoes, hematemesis and paralysis.

In addition, the present invention does not require the germanium ores to be pulverized and sintered to such high temperatures above 1,000°C, which demands considerable labor costs and manufacturing costs. Moreover, the present invention efficiently extracts oxidized organic germanium from the yellow soil and the earth from a fireplace by heating the soil in a suitable temperature range of 750 to 930°C and by heating the soil formed in a clod of earth to red heat.

Therefore, a method of manufacturing germanium-containing solution from yellow soil according to the present invention comprises: forming clods by clumping the yellow soil including earth from a fireplace; drying the clods of the soil at room temperatures for more than 24 hours or by heating them; heating the clods of the soil to

red heat at 750 to 930°C for 30 to 60 minutes; dipping the red-heated clods of the soil in water to extract oxidized germanium in a solution; and filtering the solution including the clods of the soil to produce a germanium-containing solution.

According to the present invention, it is possible to provide a method of manufacturing germanium-containing solution from yellow soil, whereby the germanium-containing solution can be obtained inexpensively and in an environment friendly manner.

Further, the present invention provides a method of manufacturing germanium-containing solution which is more economical than the above-mentioned conventional methods in terms of manufacturing processes and expenses.

DETAILED DESCRIPTION OF THE INVENTION

As described above, according to the method of manufacturing a germanium-containing solution from yellow soil of the present invention, clods are formed by clumping the yellow soil including the earth from a fireplace. Then, the clods of the soil are dried at room temperatures for more than 24 hours or dried by heating, and heated at 750 to 930°C for 30 to 60 minutes. The heated clods of the soil are then dipped in water to extract oxidized germanium, and filtered to produce a germanium-containing solution.

After the germanium-containing solution is separated out by filtering, the residue includes particulates and the yellow soil in the form of clods. The residue is stirred to be in the form of particulates, and it may be used as a raw material for cosmetics to supply oxygen to the skin. It may also be used as a moisturizing agent for the skin and as a functional material added to various products such as foods and health foods.

In the above manufacturing method, the concentration of germanium in the germanium-containing solution can be adjusted by varying the amount of the red-heated clods of the soil to be dipped in water, according to usages of interest.

The organic germanium obtained according to the present invention has no harmful effect on the human body since it is completely discharged through urine within 20 to 30 hours.

The present invention is characterized in that, instead of the natural germanium ores used in the conventional method, the yellow soil including the earth from a fireplace which is commonly available from the earth's surface is used as raw materials of the germanium-containing solution.

The yellow soil including the earth from the fireplace is used in the present invention in the form of a clod with the size of a chicken egg. If the yellow soil is not clumped in the clod, but is used as it is, it is practically very difficult to adjust the temperatures for heating the soil to red heat. That is, since individual soil particles are heated abruptly and cooled so quickly, the efficiency of the manufacturing process can deteriorate, thus reducing the efficiency of extracting germanium from the yellow soil. Therefore, by clumping the yellow soil in the present invention, it becomes easy to heat the yellow soil to red heat and becomes smooth to proceed with the entire processes, thus increasing the efficiency of extracting germanium from the yellow soil.

In the present invention, the process of clumping the yellow soil does not require any adhesives. This is because the yellow soil clumps itself by its binding property without adhesives.

Then, the clods of the yellow soil are naturally dried in an airy room for more than 24 hours or dried by heating them. The dried clods of the soil are placed in a furnace and heated to red heat at 750 to 930°C for 30 to 60 minutes.

A medium for heating to red heat may be charcoal, coal, electricity, gas, etc. Depending on the medium for heating, a suitable furnace such as charcoal kiln, fine charcoal furnace, electric furnace, gas furnace, etc. may be used.

The lower heating temperature of 750°C was chosen because the clods of the soil begin to make red-hot at the lowest 750°C and the oxidation of germanium initiates at 750°C. Further, the higher heating temperature of 930°C was chosen because germanium melts and becomes an ingot above the temperature 958.5°C (melting point) and it cannot be oxidized.

When the clods of the soil are red-heated to the above temperature range, germanium becomes unstable and is about to oxidize.

At this time, if the clods are dipped in water, the water boils and penetrates rapidly into the clods. The high-temperature heat expands the water inside of the clods,

and the water evaporates out of the clods.

At the same time, the unstable oxidized germanium in the clods flows out together with the expanded water. Therefore, a large quantity of oxidized germanium is dissolved in the water.

If the concentration of the oxidized germanium in the water is desired to be high, the amount of the red-heated clods dipped in the water could be increased.

The water including the oxidized germanium as above is then filtered to produce a germanium-containing solution.

The residue (precipitates) in the form of particulates and clods obtained after filtering is stirred and used as a functional material of various products.

The germanium-containing solution may be used as an activating material or auxiliary material for various products depending on its adaptability to a specific field and also be used as drinking water.

In order to carry out the manufacturing method of the present invention, the following apparatus and materials may be used:

A. Clods made by clumping unpolluted yellow soil on the earth's surface and the earth from a fireplace with the size of a chicken egg;

B. Furnace in which the clods of the soil are heated to red heat, i.e., electric furnace, gas furnace, charcoal kiln, fine charcoal furnace;

C. Unpolluted underground water (spring water);

D. Containers to have the above "C" therein; and

E. Filtering apparatus

In order to measure a concentration of the germanium-containing solution manufactured by the method of the present invention, the following experiment was carried out. The experimental data was obtained from the certified public analysis institute, Center for Advanced Bioseparation Techonology of INHA University.

<u>Experiment 1</u>

Conditions for extracting germanium

Standard items and conditions:

1) germanium raw ore: 1.70 kg

2) clods of yellow soil: 1.60 kg

3) water (spring water): 8 liters

4) temperature for red-heating: 750 to 930°C

5) time for heating: 30 to 60 minutes

Three samples of water and germanium-containing solutions, i.e., respectively 2 liters of standard water (spring water), water extract from the germanium raw ore, and water extract from the clods of yellow soil were prepared and analyzed as in the following Experiment 2. The latter two germanium-containing solutions were prepared according to the manufacturing method of the present invention under the above conditions.

Experiment 2

Analysis of contents of germanium

1) Analysis institute: Center for Advanced Bioseparation Techonology of INHA University

2) Equipment for analysis: ICP-M,S

3) Date of analysis: August 12, 2004

4) Analysis results:

Objects to be analyzed: Among 5 kinds of germanium existing in the natural world, i.e., Ge 70(20.55%), Ge 72(27.37%), Ge 73(7.67%), Ge 74(36.74%) and Ge 76(7.67%), only Ge 72 and Ge 74 having the highest distribution ratios were analyzed.

Ge Content			
	Ge 72	Ge 74	Ge total
standard water	1.04	0.89	1.93
extract from Ge raw ore	12.36	11.64	24.00
extract from clods of yellow soil	82.82	78.53	161.35

As described above, in the contents of two kinds of germanium, Ge 72 and Ge 74, the water extract from the clods of yellow soil showed about 160 times as much as the standard water and 7 times as much as the water extract from the germanium raw ore. Accordingly, assuming that all the five kinds of germanium were analyzed from the samples, it could be recognized that the germanium content in the water extract from the clods of yellow soil would be more than 200 times as much as the standard water.

According to the present invention, germanium-containing solution of good quality can be manufactured inexpensively and in an environment-friendly manner, without using expensive equipments and chemical materials.

Further, since the present invention uses the yellow soil including the earth from the fireplace, which is commonly available from the earth's surface, as raw materials of germanium-containing solution, instead of the natural germanium ores, it is economical in terms of manufacturing processes and expenses.